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LOW-DRIVE TEMPERATURE-STABLE MEMORY CORES

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Cambridge, Mass.

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SUMMARY

Calcium substitutions to lithium ferrite are beneficial in controlling the grain size and porosity and most likely in lowering the effective magnetic anisotropy. Memory cores made from calcium compositions have very uniform properties and offer advantages over unsubstituted lithium ferrite in memory application at excitations in the order of 350 mA. Cores of 30/18 size have been prepared from molybdenum-substituted lithium ferrite having full drive currents of 260 mA, however, the uniformity of these cores is not well established.

INTRODUCTION

Memory cores made from polycrystalline lithium ferrite tend to develop non-uniform grain growth and lose lithium during the sintering step. Non-uniformity of grain size (secondary crystallization) and variability of residual lithium content are deleterious to the uniformity and reproducibility of magnetic pulse properties. West and Blankenship (ref. 1) have used hot-pressing techniques in an attempt to reduce the loss of lithium and control grain size; however, this technique is limited in effectiveness and not readily applicable to production use. Replacement of lithium and/or iron by other cations, e.g., copper (ref. 2), manganese (ref. 3), vanadium (refs. 4, 5), and others (refs. 6, 7) has been used to improve the properties of sintered lithium ferrite. Most of the substances act as fluxes to lower the sintering temperature or as valence sinks to compensate for the loss of lithium.

This report describes the use of calcium and molybdenum as substitutes in the preparation of temperature-stable memory cores. Substituted lithium compositions which effectively improve core uniformity and lower the power required in memory application have been developed for memory cores. These improvements have been achieved by control of the ceramic structure, lowering of the coercivity, and reduction of the sintering temperature.

EXPERIMENTAL

The formulations in Table I were prepared by normal ceramic processing. Most of the compositions as prepared are lithium-rich to compensate for the loss of lithium during sintering, while not interfering with the pulse properties. The raw materials, consisting of lithium carbonate, iron oxide, calcium carbonate, and molybdenum trioxide, are "analytical grade." Each

TABLE I

COMPOSITIONS STUDIED

Formulation	Composition
A	$Li_{0.5}Ca_{0.01}Fe_{2.44}O_{3.92}$
B	$Li_{0.5}Ca_{0.01}Fe_{2.49}O_{3.995}$
C	$Li_{0.5}Ca_{0.02}Fe_{2.43}O_{3.915}$
D	$Li_{0.5}Ca_{0.03}Fe_{2.42}O_{3.910}$
E	$Li_{0.5}Ca_{0.05}Fe_{2.40}O_{3.90}$
F	$Li_{0.5}Ca_{0.10}Fe_{2.35}O_{3.875}$
G	$Li_{0.5}Fe_{2.45}O_{3.925}$
H	$Li_{0.5}Fe_{2.5}O_{4}$
I	$Li_{0.5}Mo_{0.01}Fe_{2.45}O_{3.935}$

was chemically analyzed prior to use. The weighed powders were milled in an alcohol slurry, dried, and then reacted at 700°C to decompose the carbonates and initiate spinel formation. After reaction, the powder was remilled with an organic binder in an alcohol slurry, then dried and sieved. The sieved powder was pressed into toroids at approximately 10 tons/in.^{2} to yield sintered samples of the following size: 30-mil outside diameter by 18-mil inside diameter by 6-mil height. All sinterings were carried out in platinum boats in resistance furnaces. The furnaces were equipped to control temperature, rate of rise, soak time and temperature, and rate of fall. The oxygen atmosphere was regulated by means of calibrated flowmeters.

The sintered samples were polished and heat-etched to determine the grain structure. The number of grains per unit volume was determined by the slope-intercept method assuming the average shape to be a truncated octahedron. Pulse properties were measured according to A.S.T.M. C-526-63T, "Tentative method of tests for non-metallic magnetic core to be used with a two-to-one selection ratio operating under full switching conditions." Coercivity was calculated from the current required to disturb (i.e., to cause detectable irreversible induction changes) the core under coincident-current operation.

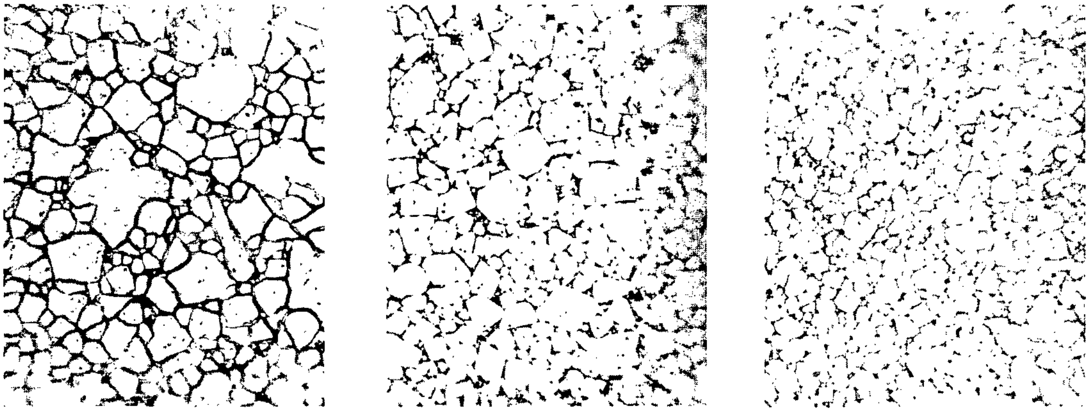
RESULTS AND DISCUSSION

Ceramic Structure

For a given sintering temperature, the influence of calcium on the grain structure is quite marked. As shown in Figure 1, the ferrites with calcium substitutions have smaller grain sizes and greater uniformity of grain size distribution. Increasing the calcium content results in decreasing the grain size as shown in Figure 2 for samples sintered at 1075 °C in oxygen. Calcium substitutions above 1.46 atomic percent result in a precipitate at the grain boundaries. Over the entire range of calcium substitutions, there is a marked decrease in the amount of secondary crystallization and a decrease in the porosity of the specimens. Increasing the sintering temperature of pure lithium ferrite results in larger grain size and a large increase in the degree of secondary crystallization. As the sintering temperature for calcium-substituted lithium ferrite increases, the grain size also increases, but secondary crystallization appears to be inhibited. The influence of calcium in lithium ferrite appears to be analogous to the influence of thorium oxide on the sintering of ytterium oxide as discussed by Jorgensen and Anderson (ref. 8).

The calcium concentration at the grain boundaries would tend to inhibit the grain boundary mobility. This inhibition of boundary would prevent the growth of large grains at the expense of smaller crystallites. The calcium at high concentration gradients at the boundaries would also act to enhance vacancy diffusion and allow the removal of pores in the grains. The higher the concentrations of calcium, the greater would be these effects (see Figure 2).

The effect of molybdenum can be considered to be that of a flux for sintering since sintering temperatures for constant grain size are reduced



1a $Li_{0.5}Fe_{2.45}O_{3.925}$

1b $Li_{0.5}Ca_{0.02}Fe_{2.43}O_{3.915}$

1c $Li_{0.5}Ca_{0.10}Fe_{2.35}O_{3.875}$

Figure 1. -- Grain structure for sintering 1 hour at 1075 °C (500X)

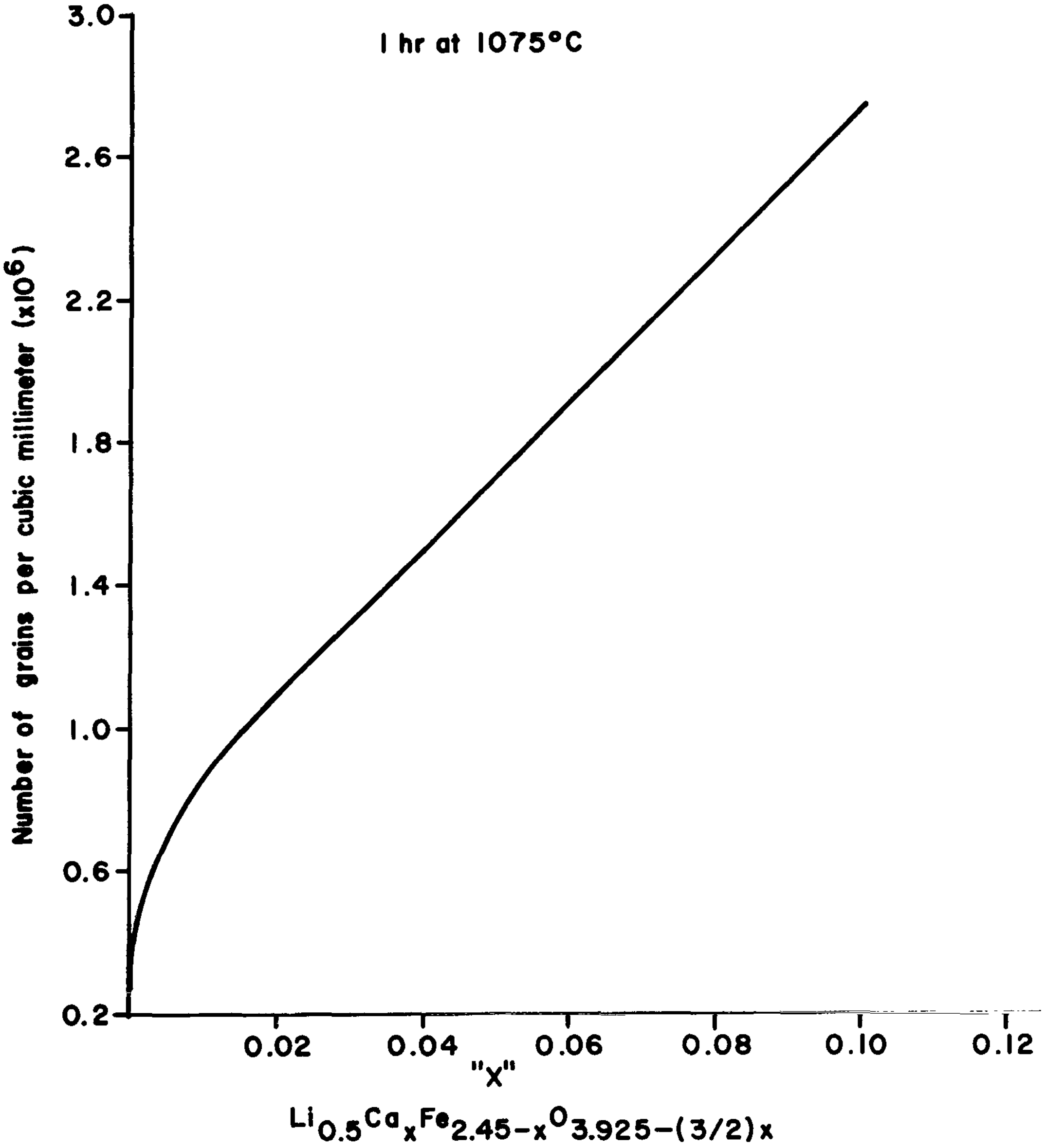


Figure 2. -- Grain size versus calcium content

for formulation I; however, there is little decrease in the porosity and secondary crystallization is quite prevalent. Both calcium and molybdenum do influence the pulse properties of lithium ferrite.

Magnetic and Pulse Properties

Calcium has a major influence on the pulse properties and the coercivity when compared to unsubstituted lithium ferrite. For a sintering of 1 hour at 1075°C, lithium ferrite (composition G) has a coercivity of 3.5 Oe and $2.7\mathrm{x}10^{5}$ grains/mm^{3}; whereas composition A has a coercivity of 1.8 Oe and $9.3\mathrm{x}10^{5}$ grains/mm^{3}. Normally the smaller grain size material, composition A, should have the higher coercivity if there were no other factors influencing magnetic properties. The results imply that the calcium substitution reduces the effective magnetic anisotropy by a factor of about 3. Composition G can be sintered to give a coercitity of 1.8 Oe; however, the number of grains per unit volume is $71\mathrm{x}10^{3}$ mm^{-3} with very extensive secondary crystallization. The uniformity of pulse properties of cores with secondary crystallization is very poor. The switching properties of the calcium-substituted lithium ferrite are quite uniform. Under similar excitation conditions such cores switch faster with higher break currents than lithium ferrite (Table II). Figure 3 shows typical pulse properties of composition B when sintered for 4 hours at 1150°C.

TABLE II

PULSE PROPERTIES OF CORES*

Formulation	uV_1 (mV)	dV_z (mV)	T_p (nsec)	T_s (nsec)	I_b (mA)
G	22	2.8	440	710	370
H	21	2.0	430	700	365
A	23	2.0	390	680	385
B	23	2.5	340	640	370
C	24	2.5	350	650	380

*(Compatible coercivity drive current = 600 mA; pulse rise time = 200 nsec; pulse duration = 1.2 msec).

The lowest drive material developed was made from composition I containing molybdenum. The coercivity is approximately 0.84 Oe for the material sintered 1 hour at 1200°C; however, yield or uniformity is quite poor because of excessive secondary crystallization. There is also substantial lithium loss at the high sintering temperature. It appears that the molybdenum can undergo changes in valence to compensate for the loss of the lithium. Typical pulse response curves for this material are shown in Figure 4 and the influence of temperature at constant excitation conditions is shown in Figure 5.

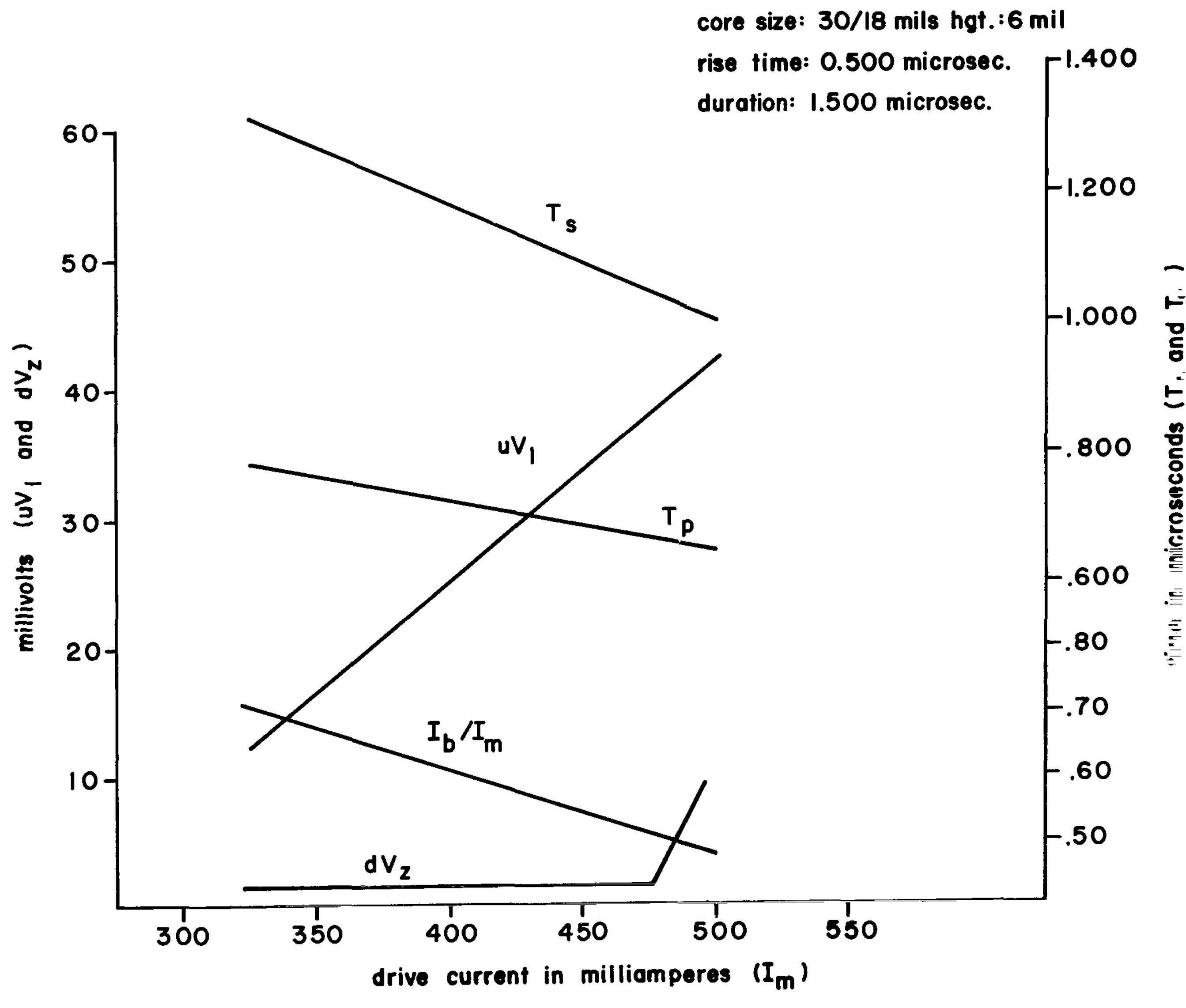


Figure 3. -- Pulse response curve of composition "B"

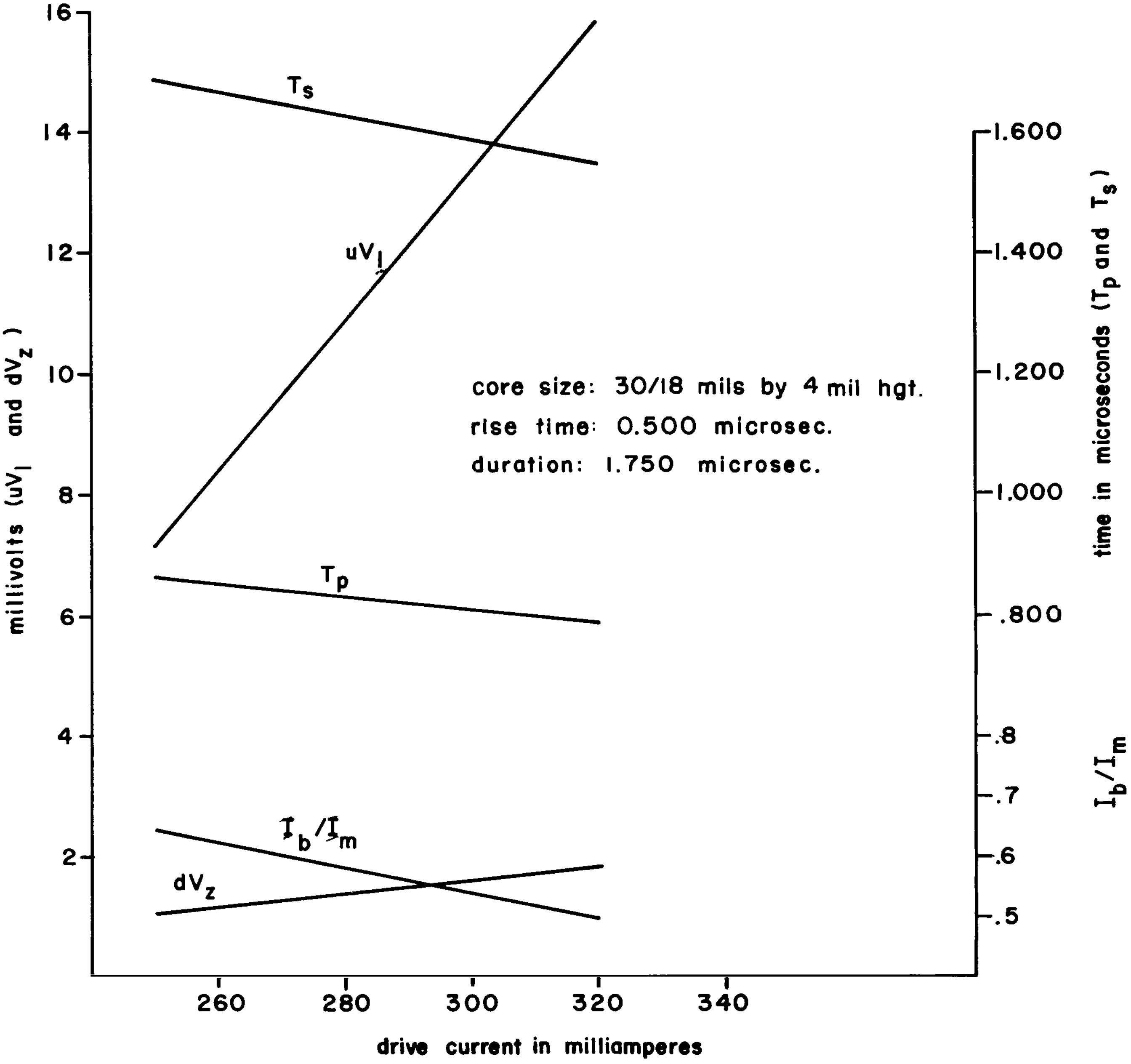


Figure 4. -- Pulse response curves of composition "I"

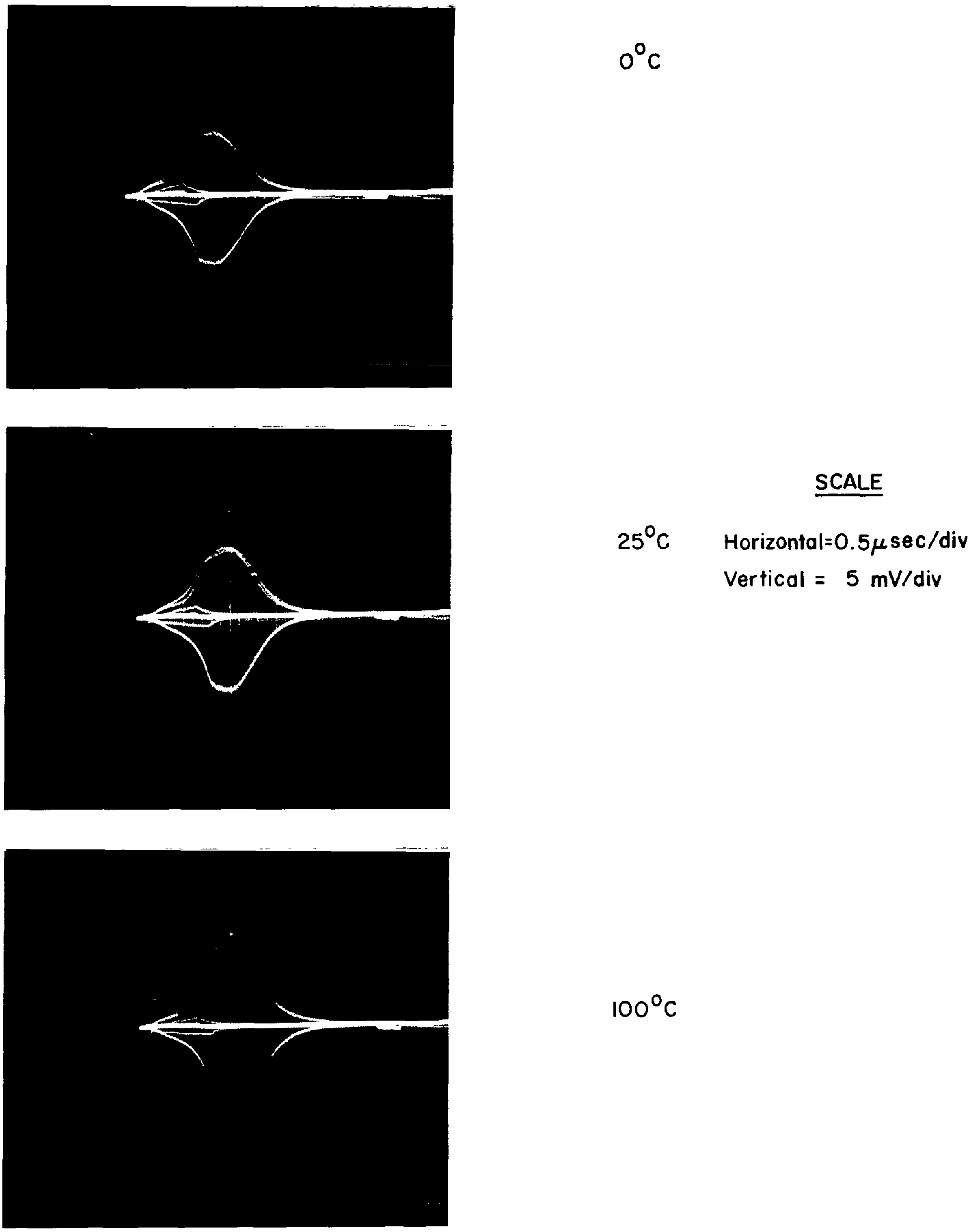


Figure 5. -- Influence of temperature on pulse response (Composition I, Drive Current=260 mA/156 mA)

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